Development of Non-platinum Electrode Catalyst for Polymer Electrolyte Fuel Cell

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論 文 内 容 要 旨

Chapter 1 : Introduction

Polymer electrode fuel cell (PEFC) is expected to use as a household and mobile scale energy systems, because PEFC works at lower temperature (<373K) than the other one. Since PEFC electrode catalyst is necessary to promote the reaction and generate, Platinum (Pt) and Pt alloys are well known as the best electrocatalyst of its anode and cathode electrode. However, because Pt is noble and expensive so that its resource is actually limited, the development of non-Pt catalyst materials is strongly required. For the promotion of PEFC performance of the Pt-alternative catalyst, the control in oxygen reduction reaction (ORR) kinetics is so important that the alternative materials have been studied to develop in pursuit of the similar activities as Pt electrode. As carbon (C) or nitrogen (N) share free electron with transition metal, they have similar properties to Pt[1]. Therefore, transition metal carbide and nitride can be used as the alternative materials. As metal combine with C, free electron transfer from metal to C. In addition, the metal lattice expands and the metal-metal distance increases by C, incorporating in the metal structure. The increased metal-metal distance causes contraction of the metal d-band. The d-band contraction leads to increase in density of states near the fermi level compare with parent metal. Therefore metal carbide has similar catalytic properties to precious metal. In addition, nanosizing of these particles is expected to enhance the catalytic activity due to the increase in surface area. From the viewpoint of interaction of the strength

between metal surface and oxygen (O) on the density of state, formation of Ni and Co carbides or borides can be applied for the electrode catalysis of ORR. Their d-band centers seem to position in near Pt or Pt compounds (E = -3.1 ~ -2.6 eV). Therefore, Ni and Co compounds were expected to show high catalytic activity. However, carbides are generally formed by carburization in CO gas or mechanical alloying. Solid-state reaction takes a long time and wastes much energy. In addition, the products contain many defects and contaminations from the erosion of milling tools. Therefore, catalytic performance of those materials on ORR has not been well known yet.

In this thesis, we will focus on the preparation of Ni and Co boride and carbide nanoparticles (NPs) for the electrode catalyst of ORR of PEFC as substitution material of Pt by use of liquid phase synthesis.

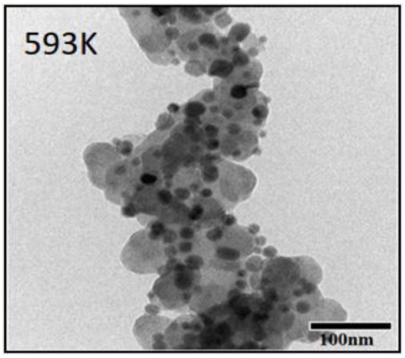

Figure 1 TEM image of as-synthesized NiC/C nanoparticles.

Chapter 2 : Preparation of Nickel boride and carbide nanoparticles on carbon carrier and their electrode catalytic activity on oxygen reduction reaction

Ni is well known as a good hydrogenation catalyst material. In particular, Ni based catalyst used on solid oxide fuel cell (SOFC). Although Ni is also used as a part of Pt alloys in PEFC on cathode, ORR performance of Ni alone is not enough high as to use as a cathode electrode. Therefore, development of Ni catalyst activity is necessary and NiB and NiC is expected to show better ORR performance.

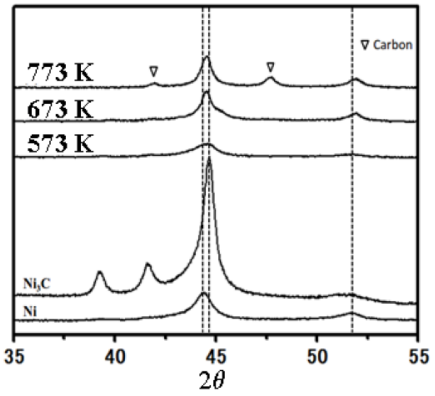

Figure 2. XRD patterns of NiC nanoparticles after heat treatment.

Ni boride NPs on C carrier (NiB) were prepared by the following procedure. $Ni(CH_3COO)_2 \cdot 4H_2O$ and C carrier was dispersed into ion exchanged water. $NaBH_4$ was added into the solution. Then, the solution was stirred for 30 min. The particles were separated by centrifugation. The crystal structure of the prepared NiB/C NPs were amorphous with composition ratio Ni : B = 90 : 10. As stable NiB structure is Ni_3B (Ni : B = 75 : 25), B ratio is small in prepared NiB structure. Because of carrier C

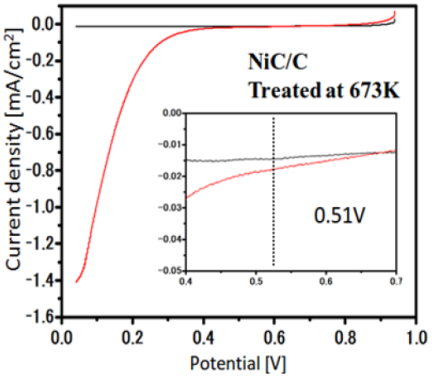

Figure 3. ORR onset potential of prepared Ni_3C/C and thermally treated Ni_3C/C.

electron negativity is bigger than B, Ni^+ connected with C and B was difficult to combine with Ni^+. In addition, B also have affinity with C, B adsorbed on carrier C and reacted with O. When the ORR performance of them was evaluated, the activity was very low compared with carrier or Ni metal NPs. In addition, the catalytic life was very short because of due to their decomposition during ORR. Therefore, the obtained NiB/C NPs were not suitable to use as an electrode catalyst on ORR of PEFC.

Ni carbide NPs on C carrier (NiC/C) were prepared by the following procedure. $Ni(acac)_2 \cdot nH_2O$ was added into oleylamine and then dissolved at 333 K for 30 min. C support added the solution and then heated up to 533 ~ 593 K under N_2 atmosphere for 1 h. The black precipitate in the solution was separated by centrifuge and then washed with hexane and ethanol. Figure 1 shows TEM image of the prepared NiC/C NPs at 593 K. The NPs with the size of 10 - 20 nm were found well dispersed on C carrier. From XRD pattern, the crystal structure was identified as hcp-Ni_3C structure. In order to enhance the catalytic activity by change of electrical structure which was operated by crystal structure, the prepared Ni_3C NPs were thermally treated in N_2 atmosphere at 673 K. After treatment, main peak shift was observed on between Ni and Ni_3C phase (Fig.2). From this shift suggested that the desorption of C from Ni_3C phase and Ni_3C phase is most stable structure among Ni-C structures, the obtained Ni-C phase might become more unstable state than Ni_3C_2. ORR performance of the prepared NiC/C NPs is summarized in Figure 3. The onset potentials of the prepared Ni/C, Ni_3C/C and annealed NiC/C NPs as their ORR activities were measured by LSV method. Formation of Ni-C structure increased ORR catalytic activity (0.36V). In addition, destabilization of electrical structure of NiC structure improved ORR performance (0.51V). The d-band center was close to Fermi Energy by thermal treatment. O desorption might be enhanced and ORR performance was increased.

Chapter 3 : Preparation of Cobalt boride and carbide nanoparticles on carbon carrier and their electrode catalytic activity on oxygen reduction reaction

In chapter 2, d-band center is increased by preparation of unstable structure. Increase of electron density might improve ORR activity. However, it is difficult to prepare Ni_2C and NiC structure. On the other hand, Co based boride and carbide have stable structures: Co_3B, Co_2B, Co_3C and Co_2C. In this chapter 3, we will focus the preparation of cobalt boride and carbide NPs. Their crystal structural stability and ORR performance are discussed. It might be higher electron density and show higher ORR

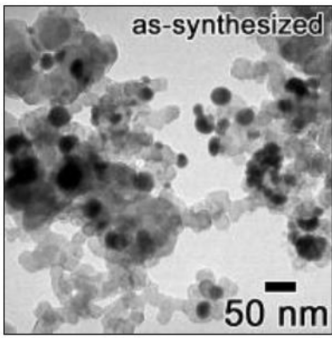

Figure 4. TEM image of CoB/C nanoparticles.

performance than Ni_3C.

Co boride NPs on C carrier (CoB/C) were prepared by the similar condition of NiB NPs. Figure 4 shows TEM image of as-synthesized CoB/C NPs. The NPs were dispersed on C carrier. Their crystal structure was amorphous. The onset potential on ORR of the NPs was low and showed similar the potential of C carrier. In addition, the CoB NPs were decomposed to metal Co and boron oxide (B_2O_3) during ORR.

On the other hand, Co carbide NPs on C carrier (CoC/C) prepared by thermal decomposition method showed higher electrode catalytic activity on ORR compared with NiB, NiC and CoB nanoparticles.

Chapter 4 : Durability of prepared boride carbide

The prepared Ni and Co borides NPs were amorphous and easily decomposed in the solution during ORR. B of the NPs was easily oxidized during ORR due to weak bond between metal and B. Therefore, increase of stability of Ni-B and Co-B should be necessary to use electrode catalyst of ORR. On the other hand, Ni and Co carbide showed higher durability compared with borides. In addition, CoC NPs showed higher catalytic activity on ORR and durability than that of NiC NPs.

Chapter 5 Conclusion

In this thesis, Ni, Co based boride, and carbide NPs on C carrier were prepared by liquid phase method. ORR activity was increased by Ni-C, Co-C combines. Co_2C/C showed higher ORR performance than the obtained Ni_3C/C and thermally treated NiC/C.

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論文審査結果の要旨

燃料電池は環境問題や化石燃料枯渇問題解決の切り札の一つとして期待されている。燃料電池の中でも固体高分子形燃料電池（PEFC）は作動温度の低さ、効率の高さから家庭用オンサイト発電への応用が期待されているが、電極触媒に枯渇の恐れがあり非常に高価な白金が大量に利用されているため、燃料電池が高価となり、普及の妨げとなっている。このような中、本論文提出者　安　昌圭　は、白金を一切利用しない空気極側電極触媒開発を目的として研究を行った。具体的には、酸素を吸着しやすく酸素還元能が貴金属に次いで高い遷移元素であるニッケルならびにコバルトを用い、これらのボライドおよびカーバイドを調製することで電子状態を変化させ、吸着の強さを制御することで、白金を一切利用しない電極触媒開発を目的とした。また、それらをナノサイズの粒子として調製することで比表面積を高くすることで活性向上を行った。

論文提出者は、材料損失が少なく、粒径制御のしやすい液相合成法を基に、求められる粒子合成のためにその条件を独自に考え最適化することで、ニッケルならびにコバルトのボライドおよびカーバイドナノ粒子を担体上へ析出させることに成功し、その粒子生成メカニズムを明らかとした点において、材料合成において、深く研究を行ったことが認められた。

得られた粒子を電気化学測定により評価し、酸素還元反応における電極触媒として作用することを確認し、その開始電位を 0.5 V 以上まで引き出すことに成功した。中でもコバルトカーバイドナノ粒子が高い酸素還元反応開始電位を発現することを発見し、コバルトカーバイドナノ粒子が電極触媒として利用可能であることを世界で初めて見出した点は、高く評価できる。

得られたコバルトカーバイドナノ粒子が高い耐久性を有することを明らかとした。他の白金代替触媒は、高い活性を有していても利用環境が高い酸性下であるため、すぐに失活してしまう。しかしながら、論文提出者が作成したコバルトカーバイドナノ粒子は、高い耐酸化性能を発現し、長期間・多回数の試験においてもその活性は維持され、高い耐久性を有することが確認された。この点は白金代替触媒の実用化への課題の一つを解決したという点で、この分野において非常に有意義な成果を出したと評価できる。

よって、本論文は博士(工学)の学位論文として合格と認める。